IC APPLICATION NOTE CIC-033

Monitoring PFASs in water sources

Non-targeted adsorbable organically bound fluorine (AOF) analysis by CIC

Per- and polyfluorinated alkyl substances (PFASs) are thousands of organic molecules in which all the hydrogen atoms on at least one carbon are replaced by fluorine [1]. PFASs are widely used in different industries, e.g., as surfactants for film-forming foams or as impregnating agents for packaging [2]. Due to their extreme persistence, they are called «forever chemicals», as longer chain compounds accumulate in the environment and biomagnify [3]. Negative health impacts have forced governmental and standardization bodies to take action against the most harmful PFASs, but suitable analytical techniques to trace and regulate these chemicals are needed. Targeted analysis of PFASs is complex and requires expensive instrumentation [4]. Conversely, determining non-targeted sum parameters is an easier way to screen for PFASs. **Adsorbable organically bound fluorine** (AOF) is a sum parameter covering a broad spectrum of organofluorines. AOF analysis is an adequate screening method for PFASs in water. DIN 38409-59 describes how to use the combination of **pyrohydrolytic combustion** and **ion chromatography** (CIC) for AOF analysis – for which Metrohm provides a robust and reliable solution.

SAMPLE AND SAMPLE PREPARATION

Three different aqueous environmental samples—one surface water and two waste waters—were analyzed for their AOF content following the procedure given in DIN 38409-59.

In contrast to other adsorbable organically bound halogens (i.e., AOCl, AOBr, and AOI), it is crucial for the determination of AOF that the samples have a neutral pH to avoid absorption of inorganic fluorine. Therefore, the samples were prepared by adding 0.5 mL of a 2 mol/L sodium nitrate solution to 100 mL sample. The adsorption of organofluorine was achieved on activated carbon as an automated sample preparation step (APU sim, Analytik Jena). Automation makes it a standardized preparation method with excellent repeatability and a high sample throughput. In short, two carbon cartridges connected in series are flushed with 100 mL sample with a flow rate of 3 mL/min. After adsorption, the two carbon cartridges are washed with 25 mL of a 0.01 mol/L sodium nitrate solution at a flow rate of 3 mL/min. After finishing the sample preparation, the complete content of the two cartridges is transferred into two separate ceramic boats for analysis by CIC.

EXPERIMENTAL

The activated carbon containing all adsorbable organically bound fluorine is analyzed by pyrohydrolytic combustion. The CIC system consists of an autosampler for solid samples, a combustion module, an absorber module, and an ion chromatograph (IC) (**Figure 1**).

The autosampler automatically transfers the sample boats into the combustion module, where they are combusted at a temperature of 1050 °C. With the gas stream, volatilized fluorine (next to other halogens and sulfur) is transferred into the 920 Absorber Module and absorbed into the aqueous phase. Precise and automated liquid handling is done with Dosinos, transferring the aqueous sample into the IC (930 Compact IC flex) for analysis. To keep the background and limits of detection of fluorine low, it is essential to use clean chemicals which are at least of the purity grade «per analysis».

The separation of fluoride (retention time 6.2 minutes) from other halogens is achieved on a Metrosep A Supp 5 - 250/4.0 column in combination with the A Supp 5 Guard/4.0 (**Figure 2**).

Automated eluent production with the 941 Eluent Production Module enables continuous and almost unattended operation of the CIC, increasing the overall performance and analysis efficiency.

The calibration (0.01–0.5 mg/L) was performed automatically from one standard solution (sodium fluoride, 0.5 mg/L) applying the Metrohm intelligent Partial Loop Injection Technique (MiPT). A calibration range of 0.01–0.5 mg/L was achieved by the using one standard with different injection volumes (4–200 µL).

The method detection limit and the method performance were checked with standardized reference materials (4-fluorobenzoic acid) and blanks (ultrapure water) prepared in the same way as the samples and analyzed for their AOF content.

Figure 1. Combustion IC setup consisting of a 930 Compact IC flex (2.930.2560), a 920 Absorber Module (2.920.0010), a Combustion Module (Oven + ABD, 2.136.0700), and a MMS 5000 Autosampler (2.136.0800) configured for solid samples (6.7302.000).

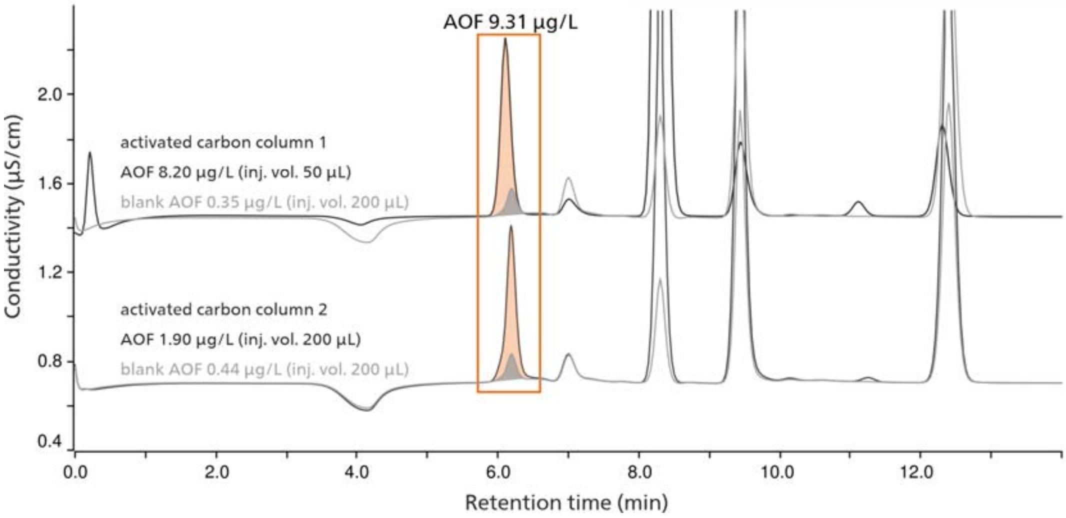

Figure 2. Chromatograms for a wastewater sample. An AOF concentration of 7.85 µg/L was found on the first carbon column and 1.46 µg/L on the second carbon column. This adds up to a total AOF concentration of 9.31 µg/L for this sample. This is the result after blank subtraction. The respective AOF blanks are also shown in grey.

The final sample concentrations are calculated according to the formula below. Thereby the final AOF concentration is the sum of the content measured for the two subsequent cartridges after blank subtraction (Figure 2).

$$c(AOF) = \left(c(F^-)_{IC} * \frac{V_{Abs}}{V_{Smpl}} \right) - \left(c(F^-_{BW})_{IC} * \frac{V_{AbsBW}}{V_{SmplBW}} \right)$$

c(AOF)	Mass concentration of AOF in µg/L
$c(F^-)_{IC}$	Fluoride concentration in the sample's absorption solution in µg/L
V_{Abs}	Final volume of the absorption solution in L
V_{Smpl}	Volume of the sample that was used for adsorption in L
$c(F^-_{BW})_{IC}$	Fluoride concentration in the absorption solution of the blank in µg/L
V_{AbsBW}	Final volume of the absorption solution of the blank in L
V_{SmplBW}	Volume of the blank solution that was used for adsorption in L

RESULTS

All samples were analyzed in replicates (n=4). All waters contained trace concentrations of AOF ranging from an average of 6.52 µg/L to 9.70 µg/L, with lower concentrations found in surface water compared to wastewater (Table 1). Although concentrations of AOF are generally low and sample preparation can be complex, the automation of sample processing and the analysis guarantees excellent repeatability. For the replicates, RSDs of 3.6–5.3% were achieved (n=4).

For routine analysis, the method blank was determined to be 1.1 µg/L for AOF (based on ultrapure water and including all sample preparation and combustion steps).

Table 1. Results of the AOF analyses for surface water and wastewater samples. The table shows AOF results for the four measured replicates of each sample, the average and standard deviation (SD), and the relative standard deviation (RSD) as determined with the formula shown above. The AOF concentrations are corrected for the blank content as required by DIN 38409-59.

Sample	AOF #1 (µg/L)	AOF #2 (µg/L)	AOF #3 (µg/L)	AOF #4 (µg/L)	Average ± SD (µg/L)	RSD (%)
Surface water	6.26	6.27	6.79	6.77	6.52±0.30	4.6
Wastewater 1	10.23	4.56	9.31	9.21	9.70±0.51	5.3
Wastewater 2	7.36	6.99	7.61	7.21	7.29±0.26	3.6

CONCLUSION

Determination of the sum parameter **AOF** according to **DIN 38409-59** enables fast and reliable **screening of PFASs** in various water samples. Ideal for monitoring, this approach can serve as a supplementary method to the comprehensive, time-consuming, and expensive targeted analysis of PFASs by e.g., LC-MS/MS. With the possibility of automated sample preparation in combination with a fully automated analysis by CIC, this is an easy, reliable, fully automated, and straightforward technique for routine AOF analysis. AOF analysis with CIC according to DIN 38409-59 is thus a fast method to monitor PFASs in water sources.

Aside from AOF, DIN 38409-59 also describes the analysis of adsorbable organically bound halogens **chlorine (AOCl)**, **bromine (AOBr)**, and **iodine (AOI)**, and the **sum of the adsorbable organically bound halogens (CIC-AOX$_{(Cl)}$)** with the same system setup and method parameters. This additionally enables laboratories to report individual, fast, and reliable results for all of these components.

REFERENCES

[1] Gehrenkemper, L.; Simon, F.; Roesch, P.; et al. Determination of Organically Bound Fluorine Sum Parameters in River Water Samples—Comparison of Combustion Ion Chromatography (CIC) and High Resolution-Continuum Source-Graphite Furnace Molecular Absorption Spectrometry (HR-CS-GFMAS). *Anal. Bioanal. Chem.* **2021**, *413* (1), 103–115. https://doi.org/10.1007/s00216-020-03010-y.

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Analytes:	**Halogens – fluorine, chlorine, bromine, iodine, organics**
Matrix:	**Water – drinking water, tap water, wastewater**
Method:	**Ion chromatography**
Industry:	**Environmental; Food & beverage; R&D (Academia)**
Standards:	**DIN 38409-59**

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